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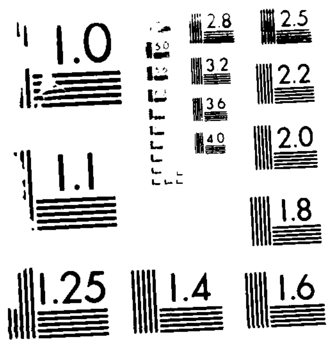

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REVERSE OSMOSIS MEMBRANE CLEANING

Research and Development Technical Final Report

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For US Army Belvoir R&D Center, Fort Belvoir, VA 22060-5606

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FOREWARD

Present technology has great difficulty maintaining the performance of reverse osmosis systems under battle conditions. This research demonstrated the technical feasibility of using ultrasonic energy to clean materials off the membrane surfaces while the reverse osmosis module was operating.

The approach involves attempting to focus sonic energy parallel to the membrane's surface. Cleaning is achieved within a few minutes by turning on a switch. Sonic cleaning appears less harsh than current chemical cleaning methods. Thus the approach may forgive errors in judgement by operating personnel.

Further research into the effectiveness of this approach is recommended.

CONTENTS

ILLUSTRATIONS

1.0 INTRODUCTION

Despite the best efforts of field personnel, all reverse osmosis (RO) systems experience fouling. The mechanisms for fouling buildup and the appropriate chemical treatments have been extensively studied. Typically combinations of detergent and citric acid are periodically used to solubilize fouling materials. Unfortunately there is evidence that current cleaning procedures may have an adverse effect on the performance of RO elements. This report deals with an alternative mechanical procedure which may have certain advantages over current chemical cleaning methods.

Any truely useful procedure should:

- forgive operator errors
- be easy to install in existant modules
- be deployable under military conditions
- be compact
- be maintenance free
- resist biological fouling
- be reliable over a wide range of operating conditions.

This research explored the feasibility of using sonic and ultrasonic treatment to clean fouled spiral wound membranes *in situ*.

The approach is to mount an array of small ultrasonic transducers flush to the outside of the pressure housing which holds the spiral wound RO membrane. The transducers are electrically driven so as to stimulate sloshing modes within the housing. Low frequency amplitude modulation of the ultrasonic transducers slowly moves the regions of most intense cleaning over the membrane surface. Experimentally a spiral wound membrane totally fouled with organic material was cleaned *in situ* merely by turning on this form of membrane cleaning for a few minutes.

This research was funded through the 1985 DoD SBIR program which is structured in three phases:

I. A three-quarter man-year effort to determine, insofar as possible, the technical feasibility of cleaning spiral wound reverse osmosis membranes *in situ* with sonic cleaning,

II. A two man-year effort to further demonstrate the effectiveness of sonic cleaning under a wide variety of potentially fouling conditions, and

III. A non-Federal program to pursue commercial applications of this R&D.

This report summarizes the Phase I research performed to demonstrate the feasibility of the proposed approach.

2.0 THEORETICAL CONSIDERATIONS

Previous work by Kuepper[1] at the Naval Civil Engineering Laboratory concluded that ultrasonic cleaning is a viable and desirable method for cleaning pieces of RO membrane. Ultrasonic cleaning effectively removes foulant from pieces of membrane that have been subjected to highly fouling feedwaters. However, these benefits were not observed in spiral-wound RO configurations, even when the modules were fabricated with materials that had relatively high sound transmission rates both when tested individually and in stacks of the spiral-wound components.

These contradictory results may be explained by the cylindrically symmetric geometry used in the Navy's tests. This geometry is shown schematically in Figure 1.

The natural acoustic resonance of a stainless steel cylinder about 4 inches in diameter filled with water is about 20kHz. This corresponds to the first radial mode in which the pressure changes are a maximum along the centerline and the node is located in a cylindrical region about halfway between the centerline and the stainless steel housing. This geometry in the first radial mode is noted for very large Qs. Because the resonant frequency of this system is so close to the 20kHz ultrasonic waves used to drive the cylindrical transducer in the radial mode, it is not surprising that Kuepper was able to melt the high-temperature PVC permeate tube while not substantially cleaning the spiral wound membrane. In his experiments most of the RO membrane was located near the node where very little if any sound energy was focused. Refabricating the spiral-wound modules with materials of higher transmission rates also had little effect, presumably because the transmission rate that sets the resonance is already set primarily by the water.

All commercially available spiral-wound RO modules are cylindrically symmetric and not much can be done about this. However, it is at least theoretically possible to excite sloshing modes within cylindrically symmetric geometries and thus to focus the sound energy so as to produce motions parallel to the RO membrane surface. Unlike radial modes, sloshing modes slosh back and forth inside the cylindrical cavity. Solutions of the wave equation in cylindrical coordinates lead to the conclusion[2] that waves can be made to travel close to the curved walls of the spiral; these waves have little motion near the cylindrical axis. The energy in these waves is very strongly absorbed by material

on the curved walls; this contrasts with radial waves which move perpendicular to the membrane and are least absorbed by material on the membrane surfaces.

For these reasons, this research involved attempting to excite sloshing modes within the pressure housing of an operating, commercially available, spiral wound RO module. The theoretical solution of the wave equation for rigid walls results in characteristic resonant frequencies.[2] The lowest sloshing frequency takes place at 0.293 c/a which for water (c = 1500m/s) and for 2.8 inch diameter (a = .036m) modules becomes about 12kHz. Thus it should be possible by placing pairs of ultrasonic transducers on either side of the cylinder and by driving them at ultrasonic frequencies but 180° out of phase to excite sloshing modes in the housing.

3.0 TRANSDUCER FABRICATION TECHNIQUES

3.1 TRANSDUCER SELECTION

A large number of piezoelectric materials are available in a variety of compositions having a wide range of properties to better satisfy the diverse applications of piezoelectric transducers. Of these, lead zirconate-lead titanate (PZT) ceramic plates were chosen for their availability and for their ability to withstand high levels of electrical excitation and mechanical stress.

Specifically forty PZT-4 strips 8.4cm long, 0.5cm wide and 0.10cm thick were purchased from Vernitron Piezoelectric Division, Bedford, Ohio. Both sides of these strips were coated with silver electrodes. The ceramic was polarized so that when these two silver electrodes were connected to an AC voltage source the plate's thickness expanded and contracted. The resonant frequency of the plates was about 2MHz. This is well above the operating frequency range of subsequent experiments.

3.2 TRANSDUCER DESIGN

The forty strips were electrically connected end-to-end to form eight identical transducers, each about 46 cm long (18in).

The electrical connections were made by soldering pairs of 1 cm long jumper wires from one electrode to the next so as to connect 5 PZT strips in parallel. Electrical solder (40/60 Sn/Pb rosin core) was used with good results. Insulated wires were connected to the two electrodes at one end of the transducer.

3.3 TRANSDUCER GEOMETRY

These eight transducers were bonded symmetrically lengthwise onto the outside surface of a PVC pressure housing by fiberglassing the transducers directly to the housing. This involved first epoxying the transducers to the PVC housing and then spiral winding fiberglass soaked in resin over the transducers. After curing this arrangement insulated the transducers as well as protected them and their connections from mechanical and environmental abuse.

A cross section view of the transducers mounted on the housing is shown in Figure 2. The diameter after fiberglassing was about 3 inches; the outer diameter of the PVC housing was 3 inches; the inner diameter of the housing was 2 5/8 inches. The eight transducers were mounted every 45^{o} around the housing. All of the 40 strips were polarized so that positive voltage applied to the outer electrode expanded the strip's thickness.

4.0 ELECTRONIC CONSIDERATIONS AND MEASUREMENTS

4.1 CONSTANT AMPLITUDE OPERATION

For non-resonant piezoelectric devices the electrical impedance of the device may be considered to be purely capacitive. For all frequencies well below the first mechanical resonance of the transducers (2MHz), the electromechanical relationships are such that the displacement of the transducer from its normal position, at any instant, is directly proportional to the electric charge applied at that instant. From the relationship that voltage = charge/capacitance, it follows that instantaneous displacement is also directly proportional to the instantaneous applied voltage.

"Constant amplitude" operation occurs when the transducer is driven by a low impedance or "constant voltage" source. For these experiments a 125 watt power amplifier was driven by Krohn-Hite arbitrary function generator. This allowed delivery of arbitrary waveforms at powers up to 125 watts over the range of 1Hz to 40kHz without distortion. The power amplifier was capable of voltage outputs of up to 150V peak-to-peak.

It should be noted that during "constant amplitude" operation, the velocity of the wall is proportional to the driving frequency.

4.2 DRIVING CIRCUIT

A block diagram of the circuit used for RO membrane cleaning is shown in Figure 3. Two separate problems are involved; namely,

How do you excite sloshing modes?
How do you cause these modes to slowly move around and around the inside of the housing?

The first problem is readily solved by placing the driving transducers on either side of the housing and by driving them 180° out of phase. This sets up wave patterns with maximum amplitudes near the transducers and minimum amplitudes near the plane of symmetry halfway between the transducers.

Solution of the second problem was achieved by first feeding the output of the power amplifier to a 4-stage relay bank. These relays are connected to the four pairs of transducers. The amplifier input is shut-down approximately 100 microseconds before and 10 microseconds after transducer pair selection in order to eliminate the effects of relay contact bounce.

The relays switch the power from one pair of transducers to the next. They are powered by a circuit which is driven by a separate signal generator whose signal can be varied from 0.1Hz to 20kHz. Thus the rate at which the sloshing modes move around the inside of the pressure housing is totally independent of the amplitude and frequency of these modes.

5.0 EXPERIMENTAL RESULTS

5.1 CLEANING OF MEMBRANE PIECES

The laboratory tests of membrane performance in reverse osmosis were performed in a 47 mm in-line stainless filter holder (Millipore XX44-047-00). It was arranged so that the feed solution containing fouling materials could be pumped into the cell holding the membrane sample. Pressure was regulated with a purge valve and fouling characteristics of 47 mm disks of membrane material were measured by monitoring the product flow rates.

Samples of membranes from Fluid Systems Division of UOP, Inc., Film Tec Corporation and Hydranautics, Inc. were tested. They were fouled with sodium chloride solutions spiked with calcium carbonate, calcium sulfate, bentonite coagulating acid and ferric oxide.

Fouled membranes were removed from the test cell, visually examined and then treated with a warm solution of 2% citric acid

and 0.1 % Triton X-100. Other samples of fouled membranes were cleaned ultrasonically in aqueous solutions of Triton X-100.

For these tests, results were nearly identical regardless of membrane manufacturer. As a consequence, results will be presented as if only one type of membrane sample had been tested.

5.2 FERRIC OXIDE TESTS

Ferric oxide (5g/l) and sodium chloride (3.0%) were kept in suspension by stirring using a magnetic stirring bar. Normal flow rates with DI water through a fresh membrane at 900 psi, regardless of manufacturer, were 0.33 ml/minute. Conductivity measurements taken at the onset of the test were 3500μMHOS. Flow rates began to drop off within a matter of minutes. After 10 minutes, flow rates had decreased 12% and after 30 minutes a 85% decrease was observed. Membrane fouling began to level off at this point so that after 60 minutes the flow rates had dropped 90%. Sodium chloride measurements also showed a rapid decrease to 700 μMHOS after 10 minutes of pumping. No sodium chloride was observed after 20 minutes.

The membrane samples were removed from the test cell and visually inspected. They appeared uniformly coated with a layer of ferric oxide. Test samples were placed in an ultrasonic bath. After 10 minutes the membrane surface appeared nearly clean. An additonal 10 minutes in the bath did not seem to improve the appearance of the membrane surface. The membrane was observed under a microscope and seemed nearly identical to a fresh membrane sample. The membrane was retested with flow rates approaching those of a fresh membrane, i.e., 0.29 ml/min, a loss of aproximately 12%.

Fouled membrane samples were also chemically cleaned in a solution of citric acid and Triton X-100. After 10 minutes, some cleaning appeared to be taking place.

The samples were rechecked at 20 and 60 minutes. No visually appreciable change occurred after 20 minutes. The membranes were checked under a microscope. It appeared as though only spotty cleaning had taken place with some areas remaining coated with a ferric oxide layer. The membrane samples were retested and flow rates with DI water only appreached 50% of normal, i.e., 0.15 ml/min.

Both the ultrasonically cleaned and chemically cleaned membrane samples were subjected to a 3% solution of sodium chloride in DI water. The ultrasonically cleaned membranes exhibited results nearly identical to fresh membranes whereas the chemically cleaned membrane displayed a lower initial conductivity reading than would be observed with fresh membrane (2100μMHOS).

The reading dropped off to 900μMHOS after 10 minutes.

Tests were repeated with bentonite coagulating agent (2g/1.6 1 H_2O) and calcium scale (5 g/1) (carbonate and sulfate). Results were very similar to those obtained with the ferric oxide tests. Flow rates decreased rapidly as did sodium chloride conductivity readings.

Ultrasonic cleaning resulted in membranes appearing and responding like new. Chemical cleaning was not as effective in removing the built up scales. Flow rates decreased by approximately 50% after cleaning.

Sugar rejection tests were performed on membrane samples before and after various cleaning techniques in an attempt to determine whether microscopic faults had been introduced into the membrane. Results of tests by the method of Klein and Weissman[3] indicate that faults were not a problem in our test procedures. This corroborates earlier findings regarding salt rejection and flow rates in general. In fact, we were unable by simply fouling and cleaning samples to reproduce the microscopic faults or holes which we observed on RO membranes field tested by MERADCOM.

A six-inch RO module was obtained from MERADCOM, cut open and examined. Samples of the RO membrane of this module were placed in the test cell. Flow rates with DI water averaged 1.2 ml/min, four times that observed with a fresh membrane. Upon observation under the microscope, a reason for this discrepancy appeared. Many small areas on the membrane seemed to be nearly worn through as if some of the grit inside the fouled spiral wound element had abraded the membrane surface. In some cases, their were actually microscopic holes, while in other areas it seemed as though the membrane had been removed leaving behind the polymer backing.

Water containing fluorescein was used to prove this theory. A solution with an initial concentration of 0.1 ppm fluorescein was continuously recycled through a fresh membrane at 900 psi. Using a filter fluorometer, no detectible fluorescein was observed in the recycled solution after 20 minutes.

The experiment was repeated using the field tested membrane. After 20 minutes the fluorescein level had only decreased to 0.09 ppm proving that holes in the membrane surface did exist.

5.3 IN SITU ULTRASONIC CLEANING OF RO MODULES

Spiral wound elements, 2 1/2" diameter, were placed inside the pressure vessel on which the ultrasonic transducers were aligned. Solutions containing blue-green algae from a local eutrophic pond, yeast (Saccharomyces cerevisiae) and combinations of the two were pumped through the elements. Flow

rates and pressure drops were monitored as indicators of membrane fouling. Samples of the concentrate water were taken periodically for microscopic and spectroscopic analysis as an indicator of proteinaceous cell removal by the membrane and spacer surfaces.

The algae were pumped through the element for 24 hours. Upstream presure increased 8%, permeate flow decreased 23% and concentrate flow decreased 8%. A sonic cleaning mode was switched on for 5 minutes at 80 watts with a slosh period of 20 Hz and a driving frequency of 490 Hz. This low frequency corresponds to a resonant frequency of the PVC pressure housing. Visually, a cloud-like mass of algae could be seen through the clear concentrate tubing as this algae exited the module. This corresponded to a 14% increase in %T (% transmittance) over normal (non-cleaning mode) concentration output. Pressure decreased to its original level, permeate flow increased to within 1% of its original level, and within five minutes the concentrate flow increased to within 2% of its original level.

S. cerevisiae cells and algae from the previous fouling experiment were harvested via centrifugation and resuspended in 1.0 liter of tap water. Turbidity measurements were taken over time. Initial readings of 13.8% T (% transmittance) increased to 97.3% of one minute of pumping in a closed loop. At 1.25 minutes a %T reading of 0 indicated no cells or algae remained in the 1.0 liter solution. At this point, the sonic cleaning cycle was initiated. The table on the next page demonstrates the dramatic effect this cleaning had on the RO element.

This table illustrates that turbidity as measured from the concentrate outflow increases as early as 30 seconds after the cleaning cycle has been initiated. At the 45 second to 1 minute mark, the highest levels of turbidity are reached, higher in fact than original levels. This indicates that material lodged from pervious fouling attempts had been dislodged during this cleaning cycle. Turbidity generally decreases steadily and quickly after 1.5 minutes implying that sonic cleaning is effective and complete within a very short period of time. Both permeate and concentrate flow rates returned to normal (normal equals rates obtained with a fresh element) within 10 minutes of beginning the cleaning cycle.

Similar experiments repeated on two other occasions produced nearly identical results.

Monitoring Concentrate Line

Time (minutes)	% T	
0	13.8	Note: %T; the smaller the number the greater the turbidity
:15	45.7	
:30	83.0	
:45	93.5	
1:00	97.3	
1:15	0	
Initiate cleaning cycle		
:15	83.0	
:30	18.2	
:45	5.6	Probably dislodged other material previously lodged in membrane from earlier fouling attempts.
1:00	5.6	
1:15	15.1	
1:30	33.7	
1:45	53.1	
2:00	67.3	
2:15	72.5	
2:30	52.5	
2:45	43.9	
3:00	67.8	
4:00	45.2	
5:00	56.9	
6:00	60.2	

TABLE 1. TURBIDITY CHANGES IN CONCENTRATE DUE TO SONIC CLEANING

In an attempt to rapidly foul a spiral wound element and thereby facilitate more cleaning cycles, solutions of sodium alginate were employed. A 6% solution was pumped in a closed loop for 60 minutes. The concentrate flow rate decreased by 66% within this time frame. An attempt at sonic and ultrasonic cleaning proved ineffective as did back flushing and a chemical cleaning solution used to remove organic substances and microbiological slimes consisting of borax, sodium salt of EDTA and trisodium phosphate.

The element was removed from the pressure vessel for observation. The thick slurry of sodium alginate had quite effectively clogged the feed end of the element. Fouling, it appeared, could not be unduly hastened. As a result, subsequent fouling tests used only more dilute solutions of algae and yeast cells applied over days.

Additional tests were conducted utilizing ultrasonic energy for cleaning. It so happens that the resonant frequency of the element and pressure vessel in the first sloshing mode was about 14kHz. This resonance was measured by using a pair of transducers as sensors and by driving the remaining three pairs so as to excite sloshing modes. Tests at 14 kHz were inconclusive; it is difficult to make quantitatitive observations of the beer-like froth produced in the concentrate.

Attempts were also made to effectively clean the spiral wound modules by using backflushing and chemical techniques.

Neither attempt worked very well. A combination of algae and S. cervesisiae were pumped through the elements for a period of 24 hours. The element was then backflushed for 60 minutes while flow rate characteristics were continuously monitored. After 60 minutes only a 10% increase in concentrate flow rate was observed compared with a 98% increase in concentrate flow rate after only five minutes of sonic cleaning.

Chemical cleaning with a recycled solution used for organic fouling materials also only produced a 10 to 15% increase in concentrate flow rate after 60 minutes.

6.0 CONCLUSIONS

Tests involving the cleaning of both membrane pieces and spiral wound modules clearly point out the effectiveness of sonic and ultrasonic cleaning over other cleaning techniques. Membrane pieces displayed nearly new characteristics after treatment in an ultrasonic bath while more traditionally cleaned pieces at best yielded only 50% improvements over their fouled conditions. Even tightly wound spiral elements reacted quickly and positively to sonic and ultrasonic stimulation. Flow rates and operating

pressures returned to normal ranges within a few minutes of beginning the cleaning cycle. Backflushing and chemical cleaning attempts could not even begin to compare with the reproducible results obtained by sonic cleaning.

7.0 RECOMMENDATIONS

These preliminary results demonstrate that further work should be spent on the problem of acoustic coupling between pressure housings, enclosed membranes and enclosed volumes of fluid. The potential for developing an improved method for cleaning RO modules is in our opinion very real.

Sonic and ultrasonic cleaning have the considerable advantage that they should be equally effective on chemically different membranes. The technique is also safe, simple, rugged, lightweight and does not involve large volumes of corrosive chemicals. For the portable, mobile RO unit, chemical additives and pretreatment hardware are not as acceptable as for fixed installations and in some cases can prohibit true mobility due to chemical logistic trains and size/weight of the pretreatment equipment.

Because cleaning involves turning on a switch, the approach forgives errors in judgement by operating personnel. This important feature separates this physical cleaning method from chemical methods.

For these reasons we recommend that this approach be further studied in both 2 1/2 inch and full-size spiral wound RO modules. These Phase II studies should include a better theoretical understanding[4] of the acoustic couplings and an experimental demonstration of the effectiveness of ultrasonic cleaning under the various conditions normally experienced by RO modules. Important considerations are cost reduction of the driving elements as well as standardization of the electronic circuit needed to drive the modules.

8.0 REFERENCES

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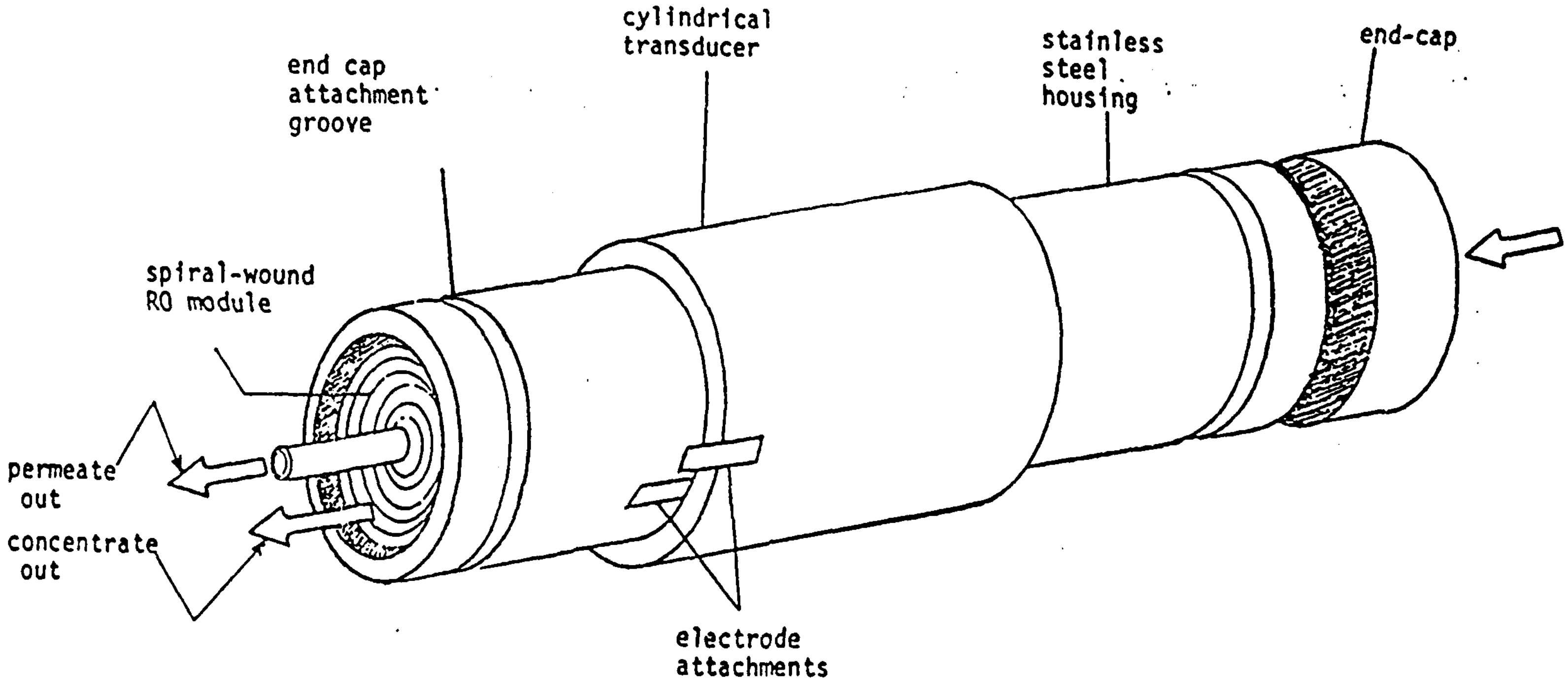

FIGURE 1. Cylindrical ultrasonic transducer mounted on RO module housing

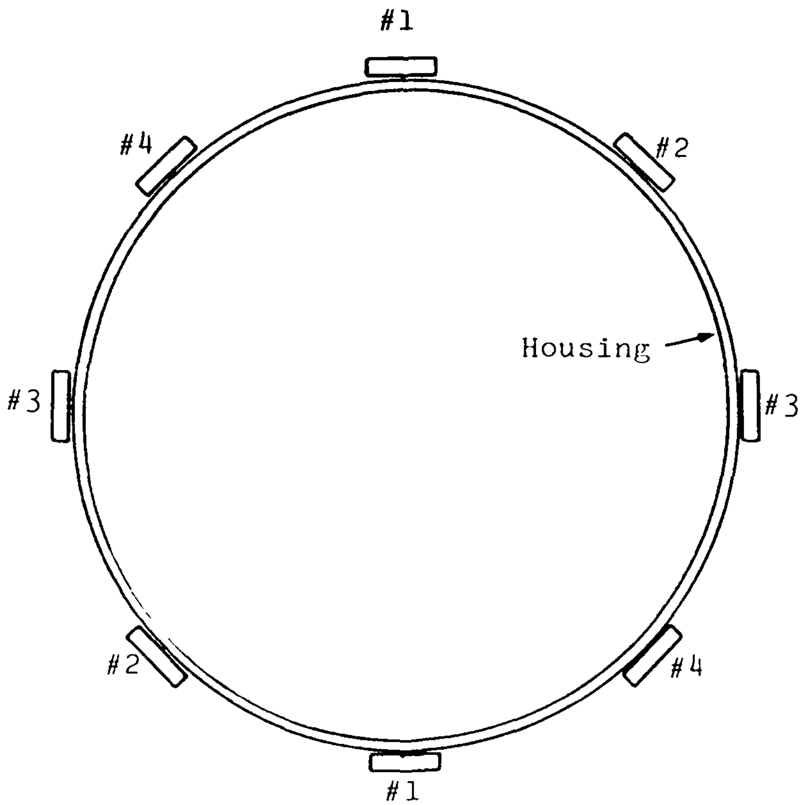

FIGURE 2. Cross section view of transducers on housing

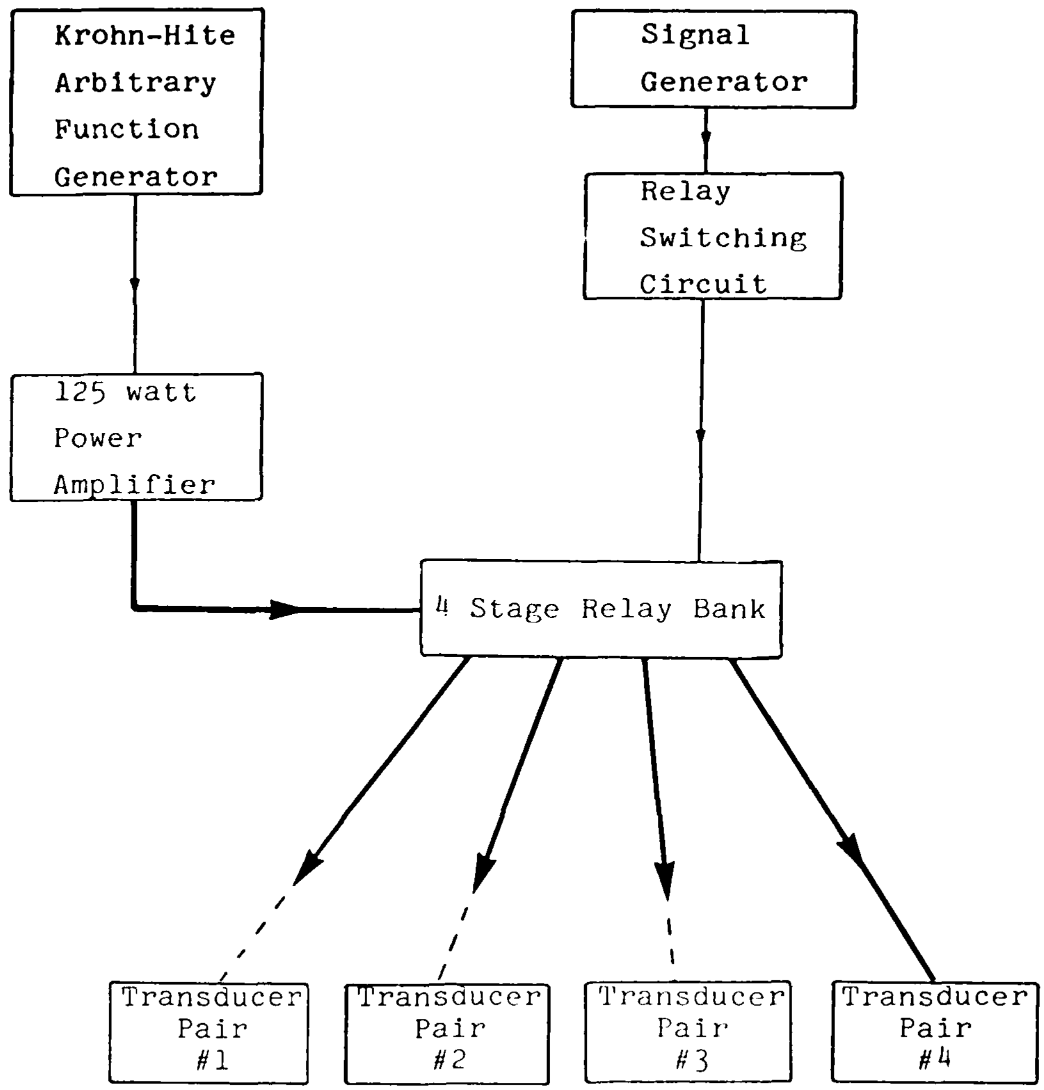

FIGURE 3. Block diagram of circuit to produce sloshing modes

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